1 **A Membrane Apparatus and Method of Preparing a**

2 **Membrane and a Method of Producing Hydrogen**

3

4 The present invention relates to a membrane and a

5 method of preparing the membrane, the membrane being

6 particularly, but not exclusively, useful in

7 producing synthetic gas for use in Fischer-Tropsch

8 gas-to-liquids production in the oil and gas

9 exploration industry or for producing hydrogen for

10 use as a fuel.

11

12 While offshore oil production has risen slightly in

13 recent years, natural gas (which mainly consists of

14 methane) production has seen a marked increase.

15 Natural gas is often extracted during the extraction

16 of liquid hydrocarbons, such as oil, from the ground

17 and is often undesirable due to the lack of

18 infrastructure to transport the natural gas to an

19 onshore location. The lack of infrastructure can be

20 explained by the physical nature of natural gas

21 which makes it difficult to transport safely and/or

22 efficiently in its basic gaseous state. As a result

1   the natural gas is often flared (ignited) causing
2   economic waste and environmental concern. It would
3   therefore be desirable to either convert the natural
4   gas into some other substance which can be
5   transported easily, or transport the natural gas in
6   a liquid state. In this way, new field development
7   will be more financially viable through the use of
8   the extensive infrastructure and technology already
9   in place in the offshore industry for transporting
10   liquid hydrocarbons.
11
12   It is known to transport natural gas as a Liquid
13   Natural Gas (LNG) in specifically constructed
14   containers onboard vessels which have been adapted
15   for such purposes. However, this has many
16   disadvantages including; the need for expensive
17   pressurising equipment which is difficult to scale
18   down to suit smaller production fields, loss of gas
19   during transportation ("boil-off"), danger posed in
20   transit to vessel and crew by high pressure, highly
21   flammable gases and the requirement to depressurise
22   the LNG into a usable gaseous state at the customer
23   end.
24
25   It is considered that a better way of utilising
26   offshore produced natural gas (CH4) is to convert
27   it, on or in close proximity to the offshore
28   production platform, into synthetic gas (syngas)
29   which can in turn be used to produce gases, fluids
30   and chemicals such as methanol, ammonia and
31   importantly, crude oil that can be readily pumped
32   through the same pipelines as the produced oil.

1   Syngas comprises a mixture of carbon monoxide(CO)
2   and hydrogen(H_2).
3
4   By way of background information to the reader,
5   conversion of syngas to liquid hydrocarbon is a
6   chain growth reaction between carbon monoxide and
7   hydrogen on the surface of a heterogeneous catalyst.
8   The catalyst is either iron or cobalt based and the
9   reaction is highly exothermic. The temperature,
10 pressure, and catalyst determine whether a light or
11 heavy syncrude is produced. For example at 330°c
12 mostly gasoline and olefins are produced whereas at
13 180°c to 250°c mostly diesel and waxes are produced.
14 There are two main types of Fischer-Tropsch
15 reactors. The vertical fixed tube type has the
16 catalyst in tubes that are cooled externally by
17 pressurised boiling water. In large plants, several
18 reactors arranged in parallel may be used,
19 presenting energy savings. Another process uses a
20 slurry reactor in which pre-heated syngas is fed
21 into the bottom of the reactor and distributed into
22 the slurry which consists of liquid wax and catalyst
23 particles. As the syngas bubbles upwards through
24 the slurry, it is diffused and converted into more
25 wax by the Fischer-Tropsch reaction. The heat
26 generated is removed through the reactors cooling
27 coils where steam is generated for use in the
28 process. Again by way of background information to
29 the reader, this is shown in Fig. 7.
30
31 Thus if methane (or other gaseous hydrocarbons)
32 could be converted to syngas and thereafter to

1   liquid hydrocarbons, the transportation costs and

2   difficulties outlined above would be mitigated.

3

4   Synthesis gas can be made by partial oxidation of

5   methane (although it is more usually made by the

6   reaction of methane with steam under pressure.)

7

8   A major safety problem with the partial oxidation of

9   methane arises because methane and air (or oxygen)

10   should be fed into the reactor at the same time and

11   therefore there is the danger of an explosion.

12

13   It is known in the art that a reactor with

14   relatively dense ceramic membranes that conduct

15   oxygen can be used for syngas production (e.g. WO

16   98/48921 and WO 01/93987). These membranes generate

17   syngas by avoiding direct contact between the oxygen

18   and hydrocarbon feed, but this necessitates the use

19   of very high temperatures in order to achieve the

20   necessary oxygen flux. Moreover, being dense means

21   that the membrane has to be as thin as possible,

22   resulting in brittleness and crack formation, loss

23   of efficiency and reduced operating service life.

24   In some cases the membrane would need to be so thin

25   that it would be unable to support its own weight

26   and therefore impossible to use in practice.

27

28   Cost effective natural gas (methane) conversion to

29   syngas for gas-to-liquids production would therefore

30   be an important commercial development.

31

1   Hydrogen can be used as a clean fuel. However, the
2   amount of hydrogen that can be produced by using
3   renewable natural energy sources such as solar,
4   wind, and hydro-power is currently not sufficient to
5   satisfy demand. The utilisation of natural gas
6   and/or the production of hydrogen from natural gas
7   seen to be a viable alternative and the most
8   realistic solution at least in the first half of
9   this century [1, 2].
10

11   An example of progress in the widespread utilisation
12   of natural gas involves the development of small co-
13   generation system using the micro-gas turbine. In
14   addition, fuel cells are expected to be a highly-
15   efficient power generating system. The fuel cells
16   are anticipated to be deployed in residences in
17   addition to the installation in electrical vehicles.
18   Home-use of fuel cells can provide hot-water and
19   electricity, simultaneously. To commercialise the
20   stationary fuel cells, it is necessary to establish
21   alternative hydrogen generation technology.
22

23   According to a first aspect of the present invention
24   there is provided an apparatus comprising a first
25   chamber and a second chamber and a membrane which
26   divides the first and second chambers; the membrane
27   comprising an inorganic support and a catalyst;
28   the membrane being adapted to allow passage of a
29   first reactant from the first chamber to the second
30   chamber through said membrane;

1   wherein the first reactant is imparted with enough

2   energy by the catalyst upon said passage so as to

3   react with the second reactant.

4

5   According to a second aspect of the present

6   invention there is provided a method of preparing a

7   membrane, the method comprising:

8   providing a support; and

9   adding a catalyst to the support.

10

11   Preferably the first reactant is activated by being

12   imparted with enough energy by the catalyst upon

13   said passage so as to react with the second

14   reactant.

15

16   Preferably the energy imparted on the first reactant

17   activates molecules of the first reactant without

18   forming an ionic species, such as O^{2-}.

19

20   Preferably the support is adapted to operate at

21   temperatures exceeding 250°C.

22

23   Preferably the support comprises an inorganic

24   support.

25

26   Preferably, the membrane initially comprises an

27   inorganic coarse porous support. Most preferably,

28   the membrane initially comprises a ceramic coarse

29   porous support such as alpha alumina.

30

1   Preferably, the first coating alters the said
2   surface of the support and more preferably, the
3   first coating roughens the said surface.
4
5   Preferably, the first coating selectively alters the
6   size, and more preferably, the diameter and
7   tortuosity of the pores. Preferably, the first
8   coating is applied by dipping the support into a
9   solution which may comprise a wash coat solution
10   such as a retracting metal oxide solution. In a
11   preferred embodiment, the wash coat solution
12   comprises Titanium Dioxide (TiO_2). Typically, the
13   first coating is applied to an outer surface which
14   may be an outer cylindrical surface of the support.
15
16   Typically, the method further includes the step of
17   applying a second coating to a second surface of the
18   support, said second surface preferably being an
19   inner surface of the support and more preferably
20   being an inner surface of a bore of the support.
21   The second coating preferably comprises a flux
22   control layer and more preferably the second coating
23   is an inorganic porous layer. Most preferably, the
24   second coating comprises a gamma alumina layer.
25   Preferably, the second coating is applied by dipping
26   the support into a solution which may comprise a
27   boehmite solution.
28
29   Typically, the method further includes the steps of
30   drying the support and heating/firing the support.
31   Typically, the dipping-drying-firing sequence of the

1   second coating may be repeated a number of times as
2   required.
3
4   Preferably, the method further includes the step of
5   applying a catalyst to a surface of the membrane.
6   Typically, the catalyst is applied to the inner bore
7   of the pores of the membrane. Typically, the
8   catalyst comprises a metallic or non-metallic
9   catalyst, and is more preferably a metallic active
10   catalyst. Most preferably, the catalyst comprises
11   active rhodium. Alternatively the catalyst can
12   comprise nickel. Preferably, the catalyst is
13   applied to the said surface by passing an osmotic
14   solution over the said first surface, which may be a
15   first side, of the membrane and a cationic or
16   anionic catalyst precursor solution over the said
17   second surface, which may be the other side of the
18   membrane, such that the catalyst is deposited on the
19   inner bore of the membrane pores. Preferably, the
20   osmotic solution comprises different electrolytes
21   and non-electrolytes in an aqueous solution at room
22   temperature. More preferably, the osmotic solution
23   comprises a sucrose solution.
24
25   Preferably, the method further includes the step of
26   heating the membrane to a relatively high
27   temperature and may include the further step of
28   passing Hydrogen through the membrane pores such
29   that calcination occurs.
30

1   Preferably, the support may comprise one or more
2   inner structures such as struts to increase the
3   surface area of the inner surface of the inner bore.
4
5   According to a third aspect of the present invention
6   there is provided a method of producing hydrogen
7   gas, the method comprising:
8   providing a membrane, the membrane comprising a
9   support and a catalyst;
10   passing a first reactant through the membrane
11   from a first chamber to a second chamber; allowing
12   the first reactant to come into contact with the
13   catalyst upon passage through said membrane;
14   imparting the first reactant with enough energy
15   so as to react with the second reactant;
16   reacting the first reactant with a second reactant
17   to produce hydrogen gas.
18
19   Preferably, the membrane comprises a substantially
20   annular cylinder and more preferably, the first and
21   second chambers comprise a substantially cylindrical
22   cross section. More preferably, a sidewall of the
23   membrane separates the first and second chambers and
24   the second cylindrical chamber may be located within
25   the first cylindrical chamber.
26
27   Preferably, the second cylindrical chamber is
28   defined by an inner bore of the membrane.
29
30   Preferably, a portion of the membrane is permeable.
31   Alternatively, the entire membrane is permeable.
32

1   Preferably, the first reactant passes from the first
2   chamber through pores formed in the sidewall of the
3   membrane to the second chamber.
4
5   Alternatively, the second reactant passes from the
6   second chamber through the membrane to the first
7   chamber.
8
9   Preferably, the first reactant is oxygen and the
10 second reactant is a hydrocarbon. More preferably
11 the second reactant is methane. Typically, the
12 synthetic gas comprises carbon monoxide and
13 hydrogen.
14
15 An embodiment of the present invention will now be
16 described, by way of example only, with reference to
17 the accompanying drawings in which:
18
19   Fig. 1 is a transverse cross sectional
20   schematic view of a support of a membrane
21   apparatus in accordance with the present
22   invention;
23   Fig. 2A is a transverse cross sectional view
24   showing the support of Fig. 1 in more detail;
25   Fig. 2B is an end view of the support of Fig.
26   2A showing 'O' rings and cross sectional shape
27   of the support;
28   Fig. 3a is a diagrammatic cross sectional view
29   showing the formation of layers in the membrane
30   of the membrane apparatus of Figs. 2A and 2B;
31   Fig. 3b is a further diagrammatic cross
32   sectional view of the membrane apparatus;

1   Fig. 3c is a yet further diagrammatic cross

2   sectional view of the membrane apparatus

3   showing the movement of molecules in use;

4   Fig. 4 is a temperature / syngas ratio plot

5   showing the optimal temperature required to

6   achieve the desired syngas ratio;

7   Fig. 5 is a feed ratio / syngas ratio plot

8   showing the optimal feed ratio required to

9   achieve the desired syngas ratio; and

10   Fig. 6 is a % Vol. N_2 / Conversion plot showing

11   conversion of CH_4 and O_2 at 750°C;

12   Fig. 7 is a schematic flow diagram providing

13   background information relating to Fischer-

14   Tropsch Gas-to-Liquids Technology;

15   Fig. 8a is a graph showing the effect of

16   temperature on the methane conversion rate;

17   Fig. 8b is a graph showing the effect of

18   reaction temperature on the conversion rate of

19   methane for fixed-bed and membrane reactors;

20   Fig. 9 is a graph showing the yield of reaction

21   products at low methane conversation rates for

22   a membrane apparatus in accordance with the

23   present invention;

24   Fig. 10 is a graph showing the yield of various

25   reaction products at high methane conversion

26   rates by varying the feed ratio at a fixed

27   temperature;

28   Fig. 11 is a graph showing the yield of various

29   reaction products by varying the temperature at

30   a fixed feed ratio;

1   Fig. 12 is a graph showing the selectivity of
2   various reaction products at low methane
3   conversions;
4   Fig. 13 is a graph showing the selectivity of
5   various reaction products by varying the feed
6   ratio at a fixed temperature;
7   Fig. 14 is a graph showing the selectivity of
8   various reaction products by varying the
9   temperature at a fixed feed ratio;
10 Fig. 15 is a graph showing the yield of various
11 reaction products against the proportion of
12 nitrogen in a nitrogen/oxygen feed;
13 Fig. 16 is a graph showing the selectivity of
14 various reaction products against the
15 percentage of nitrogen in the nitrogen/oxygen
16 feed.
17 Fig. 17 is a graph showing the yield of various
18 reaction products against the percentage of
19 carbon dioxide in the methane feed; and,
20 Fig. 18 is a graph showing the selectivity of
21 various reaction products against the
22 percentage of carbon dioxide in the methane
23 feed.
24
25 A membrane apparatus 8 in accordance with the
26 present invention is shown in Fig. 1 and comprises a
27 tubular membrane 10 and an outer tubular shell 16.
28 Two gas flow passages are thus formed which are
29 substantially sealed off from each other. The first
30 within a bore 14 of the membrane 10 and the second
31 in the annulus 22 between the membrane 10 and the
32 shell 16.

13

1   The inner bore 14 of the modified membrane 10 may

2   have some supporting struts 34, as shown in Fig. 2.

3   These increase the structural strength of the

4   modified membrane 10. In operation, the struts 34

5   also change the flow pattern of oxygen flowing

6   through the sidewall 13 of the membrane 10 by

7   reducing the opportunity for the methane flowing

8   through the inner bore 14 to pass directly through

9   the centre of the modified membrane 10 inner bore

10   without coming into contact with the modified

11   membrane 10 surface. The struts 34 also increase

12   the internal surface area per unit volume of the

13   modified membrane 10, and hence increase the

14   opportunity for activation, compared to a completely

15   hollow cross section.

16

17   With reference to Fig. 3c, the modified membrane 10

18   comprises an α-alumina support 10, a TiO_2 washcoat

19   28 on the outer surface of the support 10 and a

20   γ-alumina layer 30 on the inside of the α-alumina

21   support 10. Rh catalyst particles 12 are

22   impregnated into the bores of the inner and outer

23   face of the sidewall 13 of the modified membrane 10.

24

25   Further layers of increasing pore radii may be

26   provided adjacent to the γ-alumina layer 30 and TiO_2

27   28 layers.

28

29   Referring to Figs. 2A, 2B and 3a-3b the preparation

30   of the membrane 10 layers will now be described.

31

1 The process starts with the inorganic (preferably
2 ceramic) coarse porous support 10. Supports of this
3 nature are now widely available and a wide variety
4 of companies currently supply these base materials
5 and a preferred support 10 comprises an alpha-
6 alumina tube having 10mm outer diameter and a 7mm
7 inner diameter, typically having a pore size of
8 between 110 and 180 nm. The support 10 comprises a
9 porous middle portion 11 which is typically around
10 300 mm in length, and two remaining non-porous
11 portions 26 of about 25 mm in length at each end of
12 the membrane 10. The end portions 26 are made non-
13 porous by glazing them with a sealant, such as SiO_2-
14 BaO-CaO at 1100°C.
15
16 The wash coat 28 is then applied to the outer
17 cylindrical surface of the support 10 by dipping the
18 support 10 into a substance such as TiO_2. This wash
19 coat 28 dipping step roughens the outer cylindrical
20 surface of the support 10 and adds microporosity to
21 the walls of the membrane catalysts 12. (In
22 operation the rough surface of the wash coat 28
23 forces the oxygen particles (not shown) to convolute
24 around the raggedness of the wash coat 12 and serves
25 to improve mass transfer of the limiting reactant
26 (oxygen) to the catalytic sites - this results in
27 improved syngas yields).
28
29 The oxygen flux control layer 30 is then applied to
30 the inside surface of the inner bore 14 of the
31 support 10. This layer 30 should be inorganic to
32 enable operation of the membrane 10 at high

1   temperatures and may comprise a gamma alumina layer

2   derived from a boehmite(AlO(OH)) solution with a

3   concentration of 0.6 mol/L. The inner surface of

4   the support 10 is exposed to the boehmite solution

5   via dipping for about 2 minutes. The support is

6   then air-dried overnight and then heated to between

7   700 - 750°C at a rate of 1°C / min. It may be

8   necessary to repeat this dipping-drying-firing

9   sequence for up to a total of three cycles to

10   achieve the required gamma-alumina layer thickness

11   on the support 10.

12

13   The deposition of the catalysts 12 on the support 10

14   is achieved using an osmotic ionic exchange process,

15   which will now be described.

16

17   Osmotic Ionic Exchanged Catalyst Deposition:

18

19   The catalysts 12 are prepared using either cationic

20   or anionic exchange using RhNO3 or RhCl3.2H2O

21   respectively in an organic medium (0.2g/L) as

22   precursors. Owing to the asymmetrical character of

23   the membrane as shown in Fig. 3a (i.e. wash coat 28

24   + support 10 + gamma alumina layer (boehmite) 30)

25   different ways of introducing the catalysts 12 to

26   the support 10 are utilised. In the first instance,

27   the osmosis process involves immersing the outer

28   surface of the partially modified membrane 10 in 6.0

29   molar sucrose solution, while the catalyst precursor

30   solution (e.g. $RhNO_3$ or $RhCl_3.2H_2O$) is circulated

31   through the inner bore 14 of the partially modified

32   membrane 10. This configuration is reversed in the

1   second instance with the immersion of the outer

2   surface of the partially modified membrane 10 now in

3   a catalyst precursor solution and the osmotic

4   (sucrose) solution now circulated in the inner bore

5   14 of the partially modified membrane 10. The

6   membrane 10 is then washed using distilled water and

7   subsequently dried by blowing dry air either through

8   the inner bore of the now modified membrane 10 or

9   across the outer cylindrical surface.

10

11 Calcination (which involves heating the modified

12 membrane 10 to a very high temperature and then

13 passing Hydrogen through the modified membrane 10)

14 is then carried out under atmospheric pressure at

15 400°C for 2 hours. Metallic (active) Rh (the

16 catalyst 12) is obtained by reduction of Rhodium

17 ionic species using hydrogen at 400°C for 2 hours.

18

19 The modified membrane 10 characteristics may now be

20 measured. This may be done by scanning electron

21 microscopy (SEM) to show the degree of filling of

22 the modified membrane 10 pore network and to

23 estimate the gamma alumina (boehmite) layer 30

24 thickness.

25

26 Alternative materials may be selected. However it

27 is important that the selected materials have

28 similar thermal coefficients of expansion as

29 adjacent layers. If there is difference in thermal

30 expansion coefficients of the active porous layers

31 and porous support layers, there is an advantage in

32 selecting materials for the intermediate porous

1   support layers, with expansion coefficients which
2   gradually change from values near those for the
3   active porous layer to values near those for the
4   outer porous support layer. One way of achieving
5   this is to prepare the intermediate layers from a
6   mixture of the material used in forming active
7   porous layer decreasing in successive porous support
8   layers. For instance, porous support layer could
9   contain 75% by weight of the material used in
10 forming the active porous layer.
11
12 The above discussion does not exclude the use of
13 identical materials in active porous layer and
14 porous support layer. Such a material selection will
15 eliminate chemical incompatibility and differential
16 thermal expansion problems but typically entails
17 .sacrifices in strength and material cost.
18
19 The number of porous support layers will depend on
20 the porous radius of the adjacent active porous
21 layer. They will vary from a single layer for
22 active porous layer pore radii selected from the
23 upper end of the specified range to four for pore
24 radii selected from the lower end of the specified
25 range.
26
27 The surface area of a material determines many of
28 its physical and chemical properties, including
29 water retention capacity and reactivity with
30 nutrients and contaminants. The BET Surface Area
31 Analyser can be used to estimate the specific
32 external surface of a solid by determining the

1   volume of a specific gas that is absorbed under

2   controlled conditions. The BET surface Area

3   Analyser has typically been used in routine

4   characterisation of various membrane materials and

5   synthetic mineral analogues important in process

6   engineering systems.

7

8   In the context of the present invention, BET surface

9   area analysis using nitrogen adsorption is used to

10   estimate the pore size distribution in the modified

11   membrane 10 and also to indicate values of porosity

12   and pore volume. Energy Dispersive X-Ray Analysis

13   (EDXA) surface analysis of the modified membrane 10

14   is used to confirm whether or not the modified

15   membrane 10 forms a continuous gamma alumina network

16   and the extent of any defects. It also provides

17   elemental composition of the catalysts 12 and its

18   relative dispersion. X-ray Photoelectron

19   Spectroscopy (XPS) is then used for chemical

20   analysis of the modified membrane 10.

21

22   It is recognised that the partial oxidation of

23   methane may occur via two distinct mechanisms, i.e.

24   direct partial oxidation or total oxidation followed

25   by reforming reactions.

26

27   To convert methane to syngas a partial oxidation is

28   required.

29

30

31                   $CH_4 + O_2 \longrightarrow CO + H_2$

32
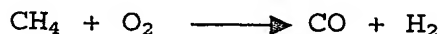
1   Should a full oxidation occur, the reaction products
2   would be CO_2 and H_2O.
3
4   The operation of the modified membrane 10 in the
5   membrane apparatus 8 will now be described.
6
7   An oxygen (O_2) supply 18 is fed into the outer bore
8   22 at one end of the membrane apparatus 8, and a
9   natural gas (which mainly comprises methane (CH_4))
10   supply 20 is fed into the corresponding end of the
11   inner bore 14.
12
13   The partial pressure of the oxygen 18 is maintained
14   at a higher pressure than that of the methane supply
15   20, which results in the oxygen passing through the
16   pores (not shown) of the modified membrane 10 from
17   the outer bore 22 to the inner bore 14. Upon doing
18   so, the oxygen molecules come into contact with the
19   catalysts 12 present in the sidewall 13 of the
20   modified membrane 10, which activates the oxygen
21   molecules before contacting the methane present in
22   the inner bore of the modified membrane 10. This
23   activation imparts sufficient energy on the O_2
24   molecule so that it can react at relatively low
25   temperatures without forming an oxygen ion.
26
27   When the activated oxygen molecules come into
28   contact with the methane molecules, syngas is
29   instantly formed according to the following chemical
30   reaction:-
31
32       $CH_4 + O_2^* \Rightarrow_{catalyst} CO + H_2$.
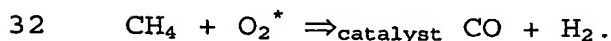
1 The produced syngas exits the membrane apparatus 8
2 from the other end of the inner bore 14 due to the
3 natural pressure differential created by the methane
4 supply 20, such that a syngas flow 24 is created.
5 Pneumatic control of the oxygen supply 18 flow rate
6 allows different flow rates of the methane supply 20
7 to be used, since an increase in the pressure of the
8 oxygen supply will result in a greater flux of
9 oxygen through the pores of the modified membrane
10 10.
11
12 In use a gas stream comprising the methane flows
13 next to or through the catalyst impregnated layer
14 12. The gamma alumina layer 30 on the bore side 14
15 enhances the reaction between permeated oxygen and
16 the methane. Since the oxygen molecules have to
17 diffuse to the bore side 14 of the gamma alumina
18 layer 30 and the adjacent porous layer, the gaseous
19 environment of the gamma alumina layer 30 at and
20 near the bore is less reducing than in the outer
21 porous layers. As a result a complete or partial
22 oxidation reaction will take place here with some
23 reforming occurring as gas moves away from the gamma
24 alumina layer 30 respectively. It is advantageous to
25 coat pores of the last porous support layer with the
26 reforming catalyst such as Rh to induce some
27 endothermic reforming as combustion products flow
28 through the porous support layer. This will assist
29 in removing the heat of the exothermic oxidation
30 reaction from the surface of the active porous
31 layer.
32

1   The gradient in oxygen activity in the porous layer

2   will prevent damage to the gamma alumina layer 30

3   from exposure to very low oxygen partial pressures,

4   thus permitting a greater degree of freedom in the

5   selection of materials for these layers.

6

7   Gas permeability through the modified membrane 10

8   can be measured by placing the end of the modified

9   membrane 10 sample tightly against the ends of the

10   outer tubular shell 16, with a seal being formed

11   therebetween by 'O' rings 32. A gas connection (not

12   shown) of the outer tubular shell 16 is attached to

13   a source of constant pressure. The predetermined

14   pressure difference being used creates a stable flow

15   of gas through the sidewall 13 of the membrane 10

16   sample, and is used to measure the flow rate, which

17   is proportional to the gas permeability of the

18   modified membrane 10.

19

20   Multi-component selectivity can be obtained by

21   measuring the individual species concentration in

22   the feed and permeate respectively.

23

24   Analysis of the reactants and products are analysed

25   using gas chromatography (GC) on-line using a 5 m

26   1/8 inch molecular sieve column to determine

27   methane, O_2, H_2 and CO. Any CO_2 will be analysed

28   using a separate 2 m long column of Porapak (RTM)

29   QS. In this analysis, a thermal conductivity

30   detector is also used. Water formed during the

31   reaction is condensed in an ice trap and further

32   removed by using a Drierite (RTM) trap.

In order to calibrate the chromatograph, multi-component gas mixtures consisting of certified compositions of methane, hydrogen, carbon dioxide, carbon monoxide and oxygen were fed on one side of the modified membrane 10 (e.g. the outer bore 22) and the streams entering and exiting the inner bore 14 were analysed using the Thermal Conductivity Detector (TCD) of a gas chromatograph.

Other aspects investigated in testing the membrane 10 include the effect of operating temperature (Fig. 4), methane flow rate (Fig. 5) and composition of syngas yield and selectivity (Figs. 4 and 6).

Figs. 9-18 show a variety of these results using such an apparatus. In each case, values of oxygen and methane conversions and the yields of hydrogen and carbon monoxide are monitored.

To investigate the initial reaction products of the CH_4/O_2 feed, experiments were carried out at low methane conversion rates and the products were analysed as detailed above.

The oxygen feed flow rate was held constant at 75ml/min and the methane feed flow rate was varied from 150 to 425ml/min, giving a range of total feed flow rates from 225 to 500ml/min. The higher total feed flow rate decreases the contact time of the reactants with the catalysts, thereby decreasing methane conversation.

1   In Fig. 8 it can be observed that for methane

2   conversion above and below 15% the CO_2 yield

3   increases significantly.

4

5   The CO yield by contrast, increases for conversions

6   lower than 20% having a slight decrease at

7   conversions around 16% increasing again thereafter.

8   The average CO yield is the highest average yield of

9   any one product. The water yield follows the same

10   profile as that for CO, but for methane conversions

11   around 18% it decreases again, deviating from the CO

12   yield. The average water yield is the lowest average

13   yield of any one product. The hydrogen yield is a

14   mirror image of the CO yield up to 16% methane

15   conversion, rising considerably for higher

16   conversion rates.

17

18   In a second experiment, the feed flow rate of oxygen

19   was varied from 15-75ml/min whilst the flow rate of

20   the methane was held constant at 150ml/min giving

21   reactions with total flow rates from 165-225ml/min,

22   as shown in Fig. 9. The temperature was 1023.15K.

23   The methane conversion decreases proportionally with

24   the increase in total flow rate, i.e. with the

25   decrease in contact time.

26

27   With higher methane conversions rates, allowing more

28   contact time, the CO_2 yield continues to increase up

29   to 30% methane conversion, falling slightly around

30   15% yield and significantly when methane conversions

31   reach around 50%. When methane conversion is over

32   55%, an insignificant yield of 5% CO_2 is found. Thus

1   the lowest yield of CO_2 is found for methane

2   conversion higher than 50%.

3

4   The CO yield stabilises at around 15% for methane

5   conversions higher than 20%. Water yield stabilises

6   at 5% for methane conversion from 20% up to around

7   40% increasing to almost 10% water yield at around

8   50% methane conversion, falling again to around 5%

9   yield at 55% methane conversion. Hydrogen yield

10   rises to around 18% hydrogen for methane conversions

11   from 30% up to 50% declining to 0.16 yield for

12   higher methane conversions.

13

14   Thus the contact time (controlled by the feed rate)

15   does not have a significant influence on the

16   resulting products, but does influence the methane

17   conversion rate. An advantage of certain

18   embodiments of the present invention is that they

19   can be used with low and high flow rates (producing

20   corresponding high and low contact times) without

21   affecting the resulting products. Longer contact

22   times aid methane conversion and provides high

23   yields of hydrogen and carbon monoxide and low

24   yields of water and carbon dioxide with methane

25   conversion is at about 50%.

26

27   To obtain this contact time the total feed flow rate

28   needs to be lower than 185ml/min for this load of

29   catalyst and temperature of 1023.15K. Other

30   embodiments of the invention can use different feed

31   flow rates.

32

1   It is well recognised that the partial oxidation of

2   methane may occur via two distinct mechanisms, i.e.,

3   direct partial oxidation or total oxidation followed

4   by reforming reactions [3]. In order to elucidate

5   the mechanism for the catalytic membrane reactor

6   used here, the effect of the temperature on the

7   methane conversion and product yields was studied.

8   The results of the analysis are presented in Figures

9   4 and 8a.

10

11   Fig. 8a shows the influence of temperature on

12   methane conversion and products yields for a total

13   feed flow rate of 165ml/min (150ml/min of methane

14   and 15ml/min of oxygen). Figure 8a shows that all

15   the oxygen is consumed. This occurs before

16   significant amounts of hydrogen and carbon monoxide

17   are formed. Another important feature is that the

18   conversion of methane, yield of water and yield of

19   hydrogen all pass through a maximum at 750°C. This

20   behaviour suggests that below 750°C, water, carbon

21   monoxide and hydrogen are primary products while

22   carbon dioxide is a parallel side reaction as

23   depicted in scheme 1.

24

25   $$CH_4 + O_2 \xrightarrow{r_1} CO + H_2 + H_2O \quad \text{Scheme 1}$$

26

27   $$\searrow^{r_2} \quad CO_2$$
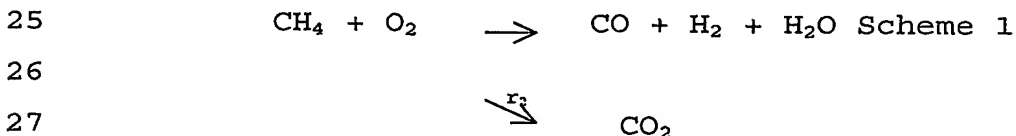
28

29   Kinetic modelling has shown that the overall

30   reaction can be described well with the contribution

31   of parallel oxidation and full oxidation according

32   to scheme 1.

1   Above 750°C, the total oxidation reaction r_2 is

2   expected to dominate with a significant increase in

3   water and carbon dioxide. However, examination of

4   Figure 8a shows that the carbon dioxide yield shows

5   only a modest increase above 750°C, while the yields

6   for water and hydrogen fall above this temperature.

7   This suggests that hydrogen, carbon dioxide and

8   water are being consumed accordingly to scheme 2

9   below.

10

11     $$CO_2 + H_2O + H_2 \xrightarrow{r_3} CH_4 + CO$$
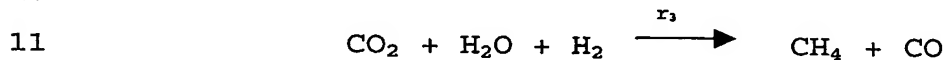
12   Scheme 2

13

14   Scheme 2 helps explain the fall in the water and

15   hydrogen yields, the modest CO_2 yield increase and

16   the fall in methane conversion above 750°C.

17

18   One important aspect in the subsequent conversion of

19   synthesis gas to liquids via a Fischer-Tropsch type

20   reaction is the hydrogen: carbon monoxide ratio. A

21   ratio of 2/1 is optimum for this conversion. From

22   examination of Fig. 4 it can be seen that an optimal

23   temperature of around 750°C results in the desired

24   syngas (H2/CO) ratio of 2.

25

26   The optimal feed ratio of methane to oxygen is

27   shown, in Fig. 5, to be 10, although reasonable

28   results which are relatively close to the desired

29   ratio of 2 are obtained at feed ratios of between 2

30   and 6 also.

31

Figure 4 shows a plot of the H_2/CO over the temperature range studied. The optimum for gas-to-liquids conversion is obtained at a temperature of 750°C. Above this temperature, a ratio below 2.0 is attained while below 750°C, a value above 2.0 is obtained.

Selectivity is defined as the yield of a particular component in proportion to the amount of methane conversion, that is

$$Selectivity_x = Yield_x / Conversion_{CH4}$$

Selectivity for low and high methane conversion rates is shown in Figs. 12 and 13. There the CO selectivity remains almost constant with values around 0.9. This possibly indicates the absence of secondary reactions for CO in low methane conversions. Hydrogen selectivity decreases for methane conversion up to 15% and increases thereafter, reaching similar CO selectivity values.

Water selectivity profile follows a mirror image of hydrogen selectivity, increasing for conversions up to 15%, decreasing for higher conversions. For higher values of methane conversion water selectivity is constant, indicating the absence of secondary reactions for water formation.

Hydrogen selectivity decreases significantly for methane conversions up to 50%, increasing slightly after that.

1   The selectivity of CO decreases to lower values than

2   H_2 selectivity for methane conversions up to 45%

3   becoming stable thereafter, indicating that for

4   methane conversions higher than 46%, CO is not

5   formed by any secondary reaction.

6

7   CO_2 selectivity decreases with the increase of

8   methane conversion, being the least selective gas

9   formed in this reaction.

10

11   It is important to note that the above-mentioned

12   experimental data were taken with varying contact

13   time, which can influence on the selectivity values.

14   For constant contact time, but varying temperature,

15   values are shown in Fig. 14.

16

17   **Effect of Feed Composition Variation on Reactor**

18   **Performance**

19

20   Figs. 15 and 16 show the yield and selectivity when

21   a varying proportion of nitrogen is added to the

22   oxygen feed. This influences the contact time of the

23   reagents with the catalyst.

24

25   Fig. 15 shows that CO yield falls constantly with

26   the addition of nitrogen in the system. Hydrogen

27   yield decreases with up to 50% nitrogen in the

28   oxygen feed and is constant thereafter.

29

30   The selectivity of carbon dioxide and water as shown

31   in the yield chart is not affected by the addition

32   of nitrogen in the system. However carbon monoxide

1   and hydrogen selectivities have a continuous drop

2   after a pick up at around 50% vol. of nitrogen.

3

4   The water and CO_2 yields values do not differ

5   significantly when nitrogen is present or absent

6   although there is a small rise for air composition

7   (80% N_2).

8

9   Fig. 6 also shows that even for an 80% vol N_2 feed

10 (and hence 20% O_2 feed) total oxygen conversion

11 takes place at a temperature of 750°C. The results

12 show that embodiments of the present invention can

13 work by using an air feed rather than a pure oxygen

14 feed thereby negating the need for an oxygen

15 separation plant for this reaction to take place.

16 This clearly reduces both the initial outlays and

17 operating costs of performing the reaction. Thus a

18 benefit of certain embodiments of the invention is

19 that air separation is not required to produce the

20 syngas of optimal ratio for onward reaction to

21 liquid hydrocarbons via a Fischer-Tropsch reaction.

22

23 In contrast to the nitrogen, the addition of CO_2 in

24 the feed does not influence CO yield, but reduces

25 hydrogen yield whilst increasing H_2O yield. The

26 results are shown in Figs. 17 and 18.

27

28 The selectivity of CO and H_2 decreases slightly in

29 higher proportion for hydrogen with the addition of

30 CO_2 in the methane feed.

31

1   The water selectivity is generally constant but does

2   increase slightly for higher amounts of CO_2 in the

3   feed.

4

5   An advantage of certain embodiments of the invention

6   is that the oxygen and methane are fed separately

7   into the apparatus and so there is no danger of an

8   explosion. The oxygen proceeds through the modified

9   membrane 10, is activated and then reacts when it

10 comes into contact with the methane. Thus it is

11 possible to lower the ratio of methane and oxygen in

12 the feed to a ratio more suitable for their

13 reaction. Such a ratio would normally be considered

14 potentially explosive, but certain embodiments of

15 the present invention allow for such ratios without

16 the potential for an explosion partly because of the

17 separate oxygen/methane feed.

18

19 Embodiments of the present invention benefit from

20 the highly dispersed catalyst which increase its

21 surface area and efficacy of the apparatus.

22

23 Embodiments of the present invention benefit from

24 the high conversion rate of oxygen. To illustrate

25 the benefits of membrane reactor operation in syngas

26 production, Figure 8b shows the effect of reaction

27 temperature on the conversion of methane over Ir-

28 loaded catalyst carried out with fixed-bed flow type

29 quartz reactor (350-10mm) at atmospheric pressure,

30 using 60mg of catalyst, 25 ml/min of O_2 and

31 temperature range of 673-873K. At 873K the

32 performance of Ir and Rh are roughly identical [4].

1   In the same figure, experimental data is shown for a

2   membrane system in accordance with the present

3   invention at 900.15K. The conversion values obtained

4   using a fixed-bed flow reactor are significantly

5   lower than those obtained in the membrane reactor

6   due to equilibrium limitation. This has been

7   overcome in the membrane reactor which achieves 100%

8   conversion of oxygen and a methane conversion of

9   41%.

10

11   Since, in the modified membrane 10, the catalysts 12

12   are highly dispersed, lower reaction temperatures

13   are feasible thereby reducing the propensity for

14   coke formation and subsequent deactivation of the

15   catalysts 12. The absence of coke formation

16   optimises catalyst usage whilst maintaining high

17   syngas selectivity. In the operation of the

18   membrane apparatus 8, additional catalysts (not

19   shown) may be inserted into the inner bore of the

20   modified membrane 10 as necessary to further enhance

21   the reaction. These additional catalysts (not

22   shown) are obtained by physically breaking another

23   sample of a modified membrane 10 into appropriate

24   particle sizes and inserting the particle sizes into

25   the test or operation sample.

26

27   Certain embodiments of the present invention benefit

28   from being used to generate hydrogen from, for

29   example, methane. The hydrogen can be used as a

30   fuel itself rather than converted into larger

31   hydrocarbons via a Fischer-Tropsch reaction.

32

1 Certain embodiments of the invention benefit from
2 the fact that the partial oxidation method is
3 exothermic and therefore reduces energy consumption.
4
5 Certain embodiments of the invention benefit from
6 the fact that the process has a fast start-up.
7
8 In contrast, steam reforming to produce syngas has a
9 large endothermic reaction and a slow start-up time.
10
11 Thus certain embodiments of the invention provide a
12 catalytic membrane reactor which has been developed
13 and used to produce hydrogen, particularly synthesis
14 gas, under various operating conditions with total
15 consumption of oxygen. At lower feed ratios (CH_4/O_2),
16 the syngas ratio is well above 2.0 while at higher
17 CH_4/O_2 ratio, the syngas ratio is 2.0. Thus depending
18 on the application the reactor is flexible to the
19 extent that it could be applied in the Fischer-
20 Tropsch process for converting natural gas to liquid
21 hydrocarbons. For gas-to-liquids conversion, an
22 optimum temperature of 750°C has been established at
23 which the hydrogen/carbon monoxide ratio is 2.0.
24
25 Modifications and improvements may be made to the
26 foregoing without departing from the scope of the
27 present invention. For example;
28
29 Though the apparatus and method described relates to
30 the production of syngas from the reaction between
31 methane and oxygen, a similar method and apparatus
32 could be used in the reaction of any light

1   hydrocarbon such as members of the alkane or alkene

2   group. Furthermore, the process and apparatus could

3   be used in any reaction where there are two

4   reactants which have constraints that make it

5   undesirable to mix them before the reaction has

6   taken place, such as flammability constraints.

7

8   It will be understood that the flux of oxygen could

9   be reversed by feeding the oxygen into the bore of

10 the modified membrane 10, and the methane into the

11 outer bore 22. However, in this case this

12 arrangement would be less desirable since the

13 methane may have impurities in it, such as H_2S,

14 which would poison the catalyst 12. Therefore

15 passing the oxygen through the modified membrane 10

16 is preferred.

1   **REFERENCES:**
2   1.   Gobina, E., *The World Natural Gas Business*,
3   BCC, Inc., 2000.
4   2.   Gobina, E., *Hydrogen as a Chemical Constituent*
5   *and as an Energy Source*, BCC, Inc. 2002.
6   3.   Prettre, M., C. Eichner, and M. Perrin, Trans.
7   Faraday Society, 1946. 43: p. 335.
8   4.   Nakagawa, K., et al., *Partial Oxidation of*
9   *Methane to Synthesis Gas with Iridium-loaded*
10   *Titania Catalyst*. Chemistry Letters, 1996: p.
11   1029-1030.
12